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**INCINERATION OF EXPLOSIVE CONTAMINATED SOIL
AS A MEANS OF SITE REMEDIATION**

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<p>Large scale releases of explosive contaminated water have occurred in connection with manufacture of explosives, with load assembly and pack operations and at centers for the disassembly and recycle of munitions. The most serious contamination is at sites where explosive contaminated "pink water" was discarded in unlined evaporation lagoons. Sediments in pink water lagoons normally contain a high concentration of explosive and contamination of ground-water is usually the result. In an effort to remediate this hazard, the U.S. Army has chosen incineration of the contaminated soil as the best means of remediation. Although there is general agreement as to the superiority of incineration for this purpose, the process is complex and environmental, legal and financial questions remain.</p>			
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Introduction

Prior to 1981 it was common practice to dispose of wastewater containing explosives in evaporation lagoons. An Army munition plant may have 6 to 10 lagoons, 1/2 acre or more in size, many of which have received wastes for over forty years. Nitroaromatic and nitramine explosives have marginal solubility in water and tend to accumulate preferentially in the upper sediment. These sediments become enriched to the extent that some contain greater than 40% explosive by weight (1). Explosives at high concentration in submerged sediments can support the formation of semi-pure crystals of explosive which may grow to several inches in diameter (2).

Contamination of this magnitude can not be contained in unlined lagoons, and leaching of explosives into aquifers becomes a likelihood. The concentration of explosive residues decreases sharply with depth but due to the extent of the contamination, excavation of 3 to 5 feet of soil is often required to meet cleanup criteria. Environmental responsibility for remediation of such sites resides wholly or partly with the US Army. Solid wastes from the production of explosives are listed as hazardous waste under 40 CFR Part 261.32 (K044, K045, K046, and K047). The wastewater and the sediments of a pinkwater lagoon meet the RCRA definition for sludge, in that they are nongaseous waste generated during wastewater treatment (40 CFR 240.101). Remediation of such contamination requires that the hazardous constituents be fixed in a stabilizing matrix or that these compounds be incinerated or otherwise destroyed.

RCRA Regulations

Either a state or a federal authority may issue and administer a permit under the Resource Conservation and Recovery Act (RCRA). The permitting authority will conduct a RCRA Facility Assessment (RFA) to determine the nature of the release and the area of contamination (AOC).

An installation which contains a pink water lagoon or other serious contamination may be required to perform a RCRA Facility Investigation (RFI). This investigation is a detailed study of the facility using available records and analytical results from soil, water and air samples. Data are examined to determine the concentration of contaminants, their potential for migration, and the environmental and public health effects. The RFI is reviewed by the governing authority to determine if remediation is needed. The approved RFI becomes part of the schedule of compliance (55 FED Reg 30801)

After completion of the RFI, a corrective measures study (CMS) is done to determine the best way to remediate the areas. The CMS outlines the possible methods which may be used for decontamination. The outline includes information on the design, construction, operation and maintenance of each method under consideration. Potential methods are evaluated for effectiveness, cost, administrative requirements, and occupational hazards (H). During the CMS phase the licensing authority may set "target" cleanup levels as a means to assess individual remediation processes.

The assessment and planning phase of the remediation is completed when a remediation method is selected and a point of compliance (POC) set by the RCRA authority. A POC is a standard of remediation usually expressed as a percent of a contaminant which is to be eliminated from the AOC. Values for POCs are included in the corrective measures implementation report (CMI) which also has the methods to be used and a timetable for permitting, setup, and restoration activities. POCs are usually chosen to reflect the best available current methods. POCs for pinkwater lagoons are on the order of 98%. Cleanup to meet this POC at the Louisiana Army Ammunition Plant (LAAP) required incineration of 100,000 tons of soil and sediment (2) and cleanup of the Cornhusker Army Ammunition Plant (CAAP) required incineration of 40,000 tons.

The LAAP and CAAP sites were restored under the interim provisions of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Remediation standards under CERCLA are consistent with the RCRA regulations but allow greater flexibility when the remediation is performed in conjunction with closure of the activity.

CERCLA Regulations

CERCLA regulations are applicable when remediation of a "hazardous waste management facility" is performed in association with installation closure. A remediation under CERCLA is initiated when a release of pollutants is reported in accordance with 40 CFR part 302 and a "removal site evaluation" is performed. The evaluation process begins with a "removal preliminary assessment". The assessment is done by the Department of Defense (DOD) acting as the CERCLA "lead agency" with federal, state and local environmental authorities as "support agencies". The preliminary assessment identifies the source, nature, magnitude and threat of the release. An assessment normally utilizes "readily available information". This information includes historical data and site management practices, photographs and personal interviews. If additional information is required a "removal site inspection" is conducted.

After completion of the removal site evaluation, the Army will decide if a "removal" action is required at the AOC. The term "removal" indicates a process which limits environmental impacts or health effects from an AOC. Severely contaminated soil, such as sediment from a pink-water lagoon will require excavation and treatment but less severe contamination may be handled by preventing access to the area or by other means. Evaluation criteria are provided in CFR 40 300.415 section b part 2. If removal is required, an engineering evaluation/cost analysis (EE/CA) may be required. An EE/CA defines the removal alternatives and is usually required only on large or unusual projects where the planning phase of the remediation lasts longer than 6 months.

If contamination levels in soil or water samples are to be determined a detailed sampling and analysis plan must be developed. The sampling and analysis plan has 2 parts, the field sampling plan, and the quality assurance project plan (QAPP). The field sampling plan describes the number, type and location of the samples to be collected and the analysis to be performed. The QAPP describes the organization objectives and the quality assurance

procedures for the sampling and analysis program. If the selected removal action does not adequately reduce the hazard the site may be subject to a "remedial" response/action.

The CERCLA remedial action process is very similar in concept to the removal action process but is more rigorous in data collection and usually leads to a more thorough remedy. The remediation starts with a "remedial preliminary assessment" (PA) this assessment is a summary of existing data including data collected in support of the removal action. Data collected at this stage is used to determine the need for further investigation and to support a later petition to include the site on the national priorities list. If the PA indicates further action is required, a remedial site inspection (SI) is initiated.

Existing data is collated and additional environmental sampling is performed as needed to provide a more complete data base on the AOC. Specifically, the remedial investigation determines the physical characteristics of the site, the classification of the waste and the environmental and health effects. Evidence of serious hazards will cause the lead agency to begin a remedial investigation/feasibility study (RI/FS) and review and update the QAPP in preparation for probable environmental reclamation at the AOC. At this point, all available information is compiled and the Army may petition the EPA to place the site on the National Priorities List (NPL) 42 CFR 300.430.

The functions of the RI/FS are to collate existing data including the results of any removal actions into a report for public release, to identify likely response scenarios, and to address the public concerns. The feasibility study also establishes the remedial action objectives and reports technical limitations and factors of uncertainty.

The most appropriate remediation method is selected by evaluating the "effectiveness, implementability and cost", of each alternative. The selection process has nine criteria for evaluation of remediation alternatives. The first two standards are the protection of human health and the environment and compliance with regulations. These are the "threshold" criteria. The remediation method must first be able to accomplish these to warrant further consideration. The "primary balancing criteria" are the long term effectiveness and permanence of the remedy, to include the reduction of toxicity, mobility or volume of contaminants and the short-term effectiveness of the method. In addition, the lead agency must consider the modifying criteria of acceptability of the procedures at the state and community level.

The remedy selection is made and the proposed plan is prepared. The plan will have a description of the remedial alternatives, the rationale for the selection and scientific comments on the method. The community must be informed of the plan and have 30 days to comment before implementation. Prior to initiation of the remediation the selection process used to determine the final remedy is documented (42 CFR 300.420) and a community relations program is established.

Incineration

Current regulations do not specify incineration as the sole method of remediation at explosive contaminated sites. However, incineration is often selected because it is the best available method for remediation of soils in which organic compounds are the principal contaminant.

When incineration is selected as the method of remediation, a "trial burn" is carried out to demonstrate the ability of the method to remove toxic compounds from the soil (40 CFR 270.62). The trial burn plan is submitted by the contractor who is performing the incineration. The application for a trial burn will include an analysis of each waste or mixture to be burned to include the amount, the heat value, and the physical characteristics. A detailed engineering description must be enclosed with the application which will describe the incinerator, the auxiliary fuel system, and the specifications of the automatic waste feed cut-off system. Information is also needed on the stack gas monitoring and pollution control equipment, the location where the unit will be set up and a description of the reaction conditions. The application must also contain critical operational procedures and a schedule for sampling and analysis of exhausts and ash (40 CFR 270.62). The trial burn will be of limited duration, and several test burns may be necessary to determine the destruction and removal efficiency (DRE) of the unit. After successful completion of the trial burn, a permit is issued and remediation is started. A formal trial burn may not be required if a similar remediation has been successfully completed at another site but the incinerator must be tested prior to use.

Operating standards for the incinerator will be set in the permit and these standards must be met throughout the operation. Incinerators burning hazardous wastes are regulated under 40 CFR 264 which stipulates principal organic hazardous constituents (POHCs) to be destroyed at a designated DRE. A DRE of at least 99.99 percent is required for each POHC, but extremely toxic compounds are further restricted under 40 CFR 264.343 part 2 to a DRE of 99.9999 percent. A separate DRE is required for each POHC in the waste stream. The POHCs for each waste stream are selected from those constituents listed in appendix VIII of 40 CFR 261 and are specified in the facility's permit. Compounds selected as POHCs need not be the most prevalent contaminants at a cleanup site; they are often selected because they are difficult to destroy or particularly hazardous. None of the common military explosives is listed in appendix VIII of 40 CFR 261, so a similar compound such as nitrobenzene, which is also present in the AOC, may be selected.

The second performance standard limits exhaust stack particulate matter. Hazardous waste incinerators which burn soil are limited to 180 mg of particulate matter per dry standard cubic meter of soil burned. This value is corrected for the amount of excess oxygen available for combustion by the formula.

$$P_c = P_m(14/(21-Y))$$

Pc is the corrected concentration; Pm is the measured concentration of particulate matter, and Y is the measured concentration of oxygen in the stack gas.

In addition, the incinerator must be able to reduce hydrogen chloride emissions to less than 1% of the chlorine present as chlorinated organics in the waste stream (40 CFR 264.342). The permit will also stipulate the permissible levels of carbon monoxide in the exhaust and reaction conditions such as temperature, feed rate, and total gas flow rate. The above factors must be continuously monitored by electronic sensing during operation. Sensors are linked to an emergency shutoff system that will automatically stop soil feed if limits are exceeded. Incinerators and associated equipment are inspected daily, and alarm systems and emergency shutdown controls are tested weekly (40 CFR 270.62).

The incineration of explosive-contaminated soils and sediments can remove hazardous organics, but this process generates a nearly equivalent volume of incinerated soil. Because of the "derived from rule", (40 CFR 261.3) incinerated soil and other residues from incineration of listed hazardous waste is initially considered hazardous waste, even though the substances which caused the soil to be hazardous have been eliminated. However the incinerated soil may be delisted if it is proven to be free of harmful characteristics. (42 USC 6921 section 3001). Delisting is important because it allows the facility to discard the incinerator wastes by land deposition at the AOC.

In accordance with 40 CFR 268.7, the "toxicity characteristic" of the incinerator waste as defined in 40 CFR 261.24 must be determined prior to its disposal by land deposition. In these determinations, representative samples of incinerator ash are extracted with water in accordance with EPA procedures outlined in appendix II of 40 CFR 261 and the concentrations of toxic compounds which become dissolved in the water are determined. Concentrations of toxic materials in the water that are in excess of RCRA standards provided in table 1 of 40 CFR 261.24 preclude the incinerator wastes from being delisted. Additional treatment to stabilize leachable toxic materials, is then required before disposal at the AOC or at an off site landfill.

Incinerator Performance

The incinerators commonly used for this purpose are two stage systems consisting of a rotary kiln primary combustion chamber and a jet type secondary burner (3). The primary and secondary chambers are heated with a high temperature propane/air flame, and additional air is introduced to both chambers to accomplish the incineration. Exhaust gases leaving the secondary chamber are cooled, and particulates are removed in an air pollution control system (bag house or wet scrubber).

The efficiency of removal of explosive residues from soil by incineration is dependent on the temperature of the primary chamber, the abundance of oxygen, and the residence time (4). Requirements vary with soil type and

moisture, but temperatures in excess of 1200 °F and quantities of oxygen 100% to 200% greater than the amount required to combust the organics in the soil are usually required for adequate performance (4).

Shortages of oxygen during incineration of explosive contaminated soils are known to produce reducing conditions which are associated with accumulation of unwanted organic compounds in the ash (4).

Products of Incomplete Combustion (PICs)

High temperatures and lean burning (excess oxygen) conditions are optimal for combustion of organic compounds. However, limitations on costs of fuel, high rates of slag formation, and generations of unwanted oxides of nitrogen require more moderate conditions. Because of these conflicting requirements operating conditions must be more moderate than those required for optimal combustion, and products of incomplete combustion are sometimes generated.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are complex aromatic compounds which result from association of organic free radicals under oxygen depleted conditions (5). PAH compounds are generated in incinerators by the incomplete combustion of organic compounds during periods of oxygen shortage. Virtually any hydrocarbon, even those as small as methane, can produce PAHs, and, once generated, PAHs exhibit substantial stability toward thermal degradation and volatilization. PAHs are toxic compounds with demonstrated carcinogenic potential (5). Brueggemann found the PAHs phenanthrene, fluoranthene, pyrene, benz(a)anthracene, benz(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene in his analysis of the organic compounds present in bag house ash from incinerators which burn munitions for demilitarization (6).

Determination of PAHs requires substantially different HPLC chromatographic conditions and detection wavelengths than those commonly used for nitroaromatic and nitramine explosives (6). Analyses to determine the presence of PAHs in the ash were not performed during the remediations thus far completed (CAAP and LAAP). However analyses for total organic carbon were performed and one may state with high assurance that conditions which minimize total organics in the incinerated soil will also minimize generation of PAHs.

Nolan et al. (4) report that compounds of carbon persist at nearly 36,000 ppm in soil incinerated at sub-optimal temperature with diminished airflow, but this value is reduced to 2,600 ppm under more vigorous conditions. Analysis of the latter soil revealed that incineration was capable of reducing the concentration of explosive residues to levels which could not be detected with conventional high performance liquid chromatography/UV (HPLC) instrumentation (< 1 ppm).

Carbon Monoxide (CO)

In addition to compounds in the ash, incomplete combustion in the rotary kiln portion of the incinerator will produce carbon monoxide (CO) in the exhaust gas. Carbon monoxide is toxic and should be removed from exhausts by vigorous oxidizing conditions in the secondary chamber. Incinerator exhausts entering the atmosphere must be continuously monitored for CO in accordance with 40 CFR 264.347. It is useful to monitor levels of CO from the primary combustion chamber (rotary kiln portion of the incinerator) because elevations in CO are indicative of incomplete combustion, which is also associated with toxic organic compounds in the ash. Carbon monoxide is an intermediate product in the stepwise oxidation of organics. It is normally anticipated that the conversion of CO to CO₂ will be the rate limiting step in an incineration. It is common for the conversion of CO to CO₂ to require 90% of the entire time required for combustion (4). Therefore, very low levels of CO in comparison to CO₂ in the exhaust from the primary chamber indicate oxidizing conditions and high combustion efficiency. It is amply documented (5) that combustion conditions such as these are not capable of generation of PAHs. Therefore, analysis of this gas prior to its reaching the after-burner provides a convenient real-time method for monitoring reaction conditions in the primary chamber. Examination of data from an incineration test in which reaction conditions were varied reveals dramatic accumulation of CO in response to low temperature low O₂ conditions. Incineration at 980°F with reduced air produced CO at 1050 ppmv in the exhaust from the primary combustion chamber. This level was reduced to as little as 5 ppmv by increases in kiln temperature and O₂ supply (4).

Combustion of compounds in the primary combustion chamber under rigorous conditions will control production of PAHs and CO but will yield a different suite of environmental contaminants.

Oxides of Nitrogen

Oxides of nitrogen (NO_x) compounds are atmospheric pollutants generated whenever oxygen and nitrogen are combusted. Higher temperatures and increased abundance of oxygen yield higher concentrations of NO_x. Experiments reported by Nolan et al (4) reveal that the highest levels of NO_x were encountered under conditions where the ratio of air and propane fuel in the flame were in stoichiometric balance and the flame temperature was at its maximum of 3,000 °F. A 10% increase in O₂ reduced the flame temperature to 2,200 °F and greatly reduced the formation of NO_x. The principal oxide of nitrogen formed during combustion is nitric oxide (NO). Nitric oxide is further oxidized after its release to yield nitrogen dioxide (NO₂) and ultimately nitrate (NO₃⁻). Nitric oxide is not toxic at concentrations normally encountered, even near incinerators, but NO₂ is an important air pollutant in urban environments. Nitrogen dioxide accumulates rapidly in polluted urban atmospheres due to the rapid oxidation of nitric oxide by ozone and is responsible for the brown color and much of the respiratory distress associated with urban air. Oxides of nitrogen are also precursors of toxic photochemical smogs, which form when these compounds react with hydrocarbon pollutants in the presence of sunlight (5).

The above problems are greatly reduced if NO_x are released in a manner that minimizes their encounter with urban atmospheres. Oxides of nitrogen released in moderate quantities into uncontaminated air will not travel great distances downwind as do oxides of sulfur (5). Under such conditions NO is slowly oxidized to NO_2 and then to nitrate, which is ultimately eliminated from the atmosphere in rainwater. Nitric acid (nitrate) contributes to the acid rain problem in regions downwind of the incinerator, but nitrate in the salt form has a short residence time in terrestrial and aquatic environments because of its status as a critical plant nutrient.

Metals

Adverse environmental impact may result from land disposal of incinerated soil which contains metals, even at concentrations which did not pose an environmental risk when present in soil or sediment. The most common compounds generated by the incineration of metals are divalent oxides. Calcium and magnesium are common Group II elements (alkaline earths); soils deficient in these compounds are rare (5). Moreover, agricultural lime (Ca(OH)_2) is added to wet soils at up to 2% to ease processing. Oxides of Group II compounds (CaO , MgO etc.) are strongly basic and are converted to soluble hydroxides by reaction with water (7). The presence of Ca(OH)_2 in incinerated soil is environmentally significant because it will elevate the alkalinity of leaches. Elevation of soil pH is predicted to reduce the aqueous solubility and rate of transport of any toxic metals which may also be present in the ash.

Toxic metals are often found in conjunction with explosive compounds, and, when present, complicate the restoration of explosive-contaminated sites. Wastes generated during metal plating and processing operations were routinely released into the pinkwater lagoons at Louisiana Army Ammunition Plant (2). The presence of toxic metals should be anticipated if the site undergoing remediation was an Army ammunition plant which manufactured the metal portions of munitions.

With the exception of mercury, toxic metals are not removed by incineration and present the greatest impediment to land disposal of incinerator ash. Chromium, cadmium, barium, and lead are the metals which are most often encountered as anthropogenic elevations at Army installations (8).

Table 1 of 40 CFR 261.24 lists the following maximum allowable concentrations of metals in aqueous leachates generated in the "toxicity characteristic" tests described above; chromium 5.0 ppm, cadmium 1.0 ppm, barium 100.0 ppm, lead 5.0 ppm, and mercury 0.2 ppm.

Mercury

Mercury is found primarily at sites which were contaminated by mercury fulminate primary explosive and also at army ammunition plants which utilized the mercury crack test in the quality control examination of munitions. The majority (92%) of the mercury in coal that is burned for generation of electricity is lost to the atmosphere as gaseous "metallic" mercury (9). Recovery of gaseous mercury from stack gas is difficult because of its

volatility at high temperatures and the difficulty of recovering an uncharged zero valence vapor from combustion exhausts (9). The volatilization of mercury from incinerated wastes is similar to the losses during the combustion of coal. Therefore the incineration of soils containing cinnabar or other forms of mercury in high concentration should be avoided.

Barium

Barium is a Group IIa compound and is strongly electropositive. It normally has a valence of +2. Soluble salts of barium are utilized as rodenticides because of their toxicity to mammals.

Barium, like calcium, forms thermally-stable, alkaline oxides when heated in air at incinerator temperatures. BaO reacts explosively with water to form a highly basic hydroxide (7). The substantial aqueous solubility of $Ba(OH)_2$ would suggest that this compound would pose a leaching hazard if exposed to rain water. Moreover, It is reasonable to assume that concentrations of $Ba(OH)_2$ in incinerator ash would enter the aqueous phase (TCLP extract) quantitatively when subjected to the EPA extraction procedure tests to determine the "toxicity characteristic" of waste materials (40 CFR 261 Appendix II). Thus, incinerated soils which contains significant anthropogenic elevations of this metal pose a leaching hazard to the environment, and will require pretreatment prior to their application to land.

Lead

The predominant species resulting from the incineration of lead are lead (II) oxide (PbO) and lead (II) halides. Lead (II) oxide can form oxide-hydroxides ($PbO \cdot H_2O$) in carbonate-free water but forms basic carbonates of lead [$PbCO_3 \cdot Pb(OH)_2$] when carbonates are present and the solution is alkaline. Both PbO and [$PbCO_3 \cdot Pb(OH)_2$] are only marginally soluble in water over the range of pHs normally found in the environment (10). Thus, it is likely that TCLP extractions of ash which contain these compounds, will not yield high concentrations of lead. However, if lead is burned in soil which contains significant levels of co-contaminants, different toxicants are possible.

Lead dihalides are generated when compounds of lead are combusted with organohalides. Dichlorolead and chloro-bromolead have significant volatility at incinerator temperatures and are the predominant form of lead in the atmosphere (5). Lead dihalides are soluble in cold water on the order of 100 g/L (11) and concentrations which remain in the ash after incineration will pose an impediment to land disposal.

Cadmium

Cadmium is oxidized to cadmium oxide upon incineration (12). Cadmium oxide is insoluble in water having neutral or elevated pH, so it would not be expected to dissolve in leaching water at environmentally significant rates. Cadmium oxide like many metal oxides can react with water to form hydroxides; however, this reaction does not proceed at a significant rate under normal

environmental conditions. Formation of cadmium hydroxide may be significant from an environmental standpoint because these compounds are marginally soluble in water (12).

Chromium

Chromium that is incinerated under vigorous oxidizing conditions forms a mixture of Cr^{+2} (CrO) and Cr^{+3} (Cr_2O_3) oxides. Compounds of chromium which exist in the 2^+ or 3^+ oxidation state have limited potential for leaching into aquifers or for accumulation in plants because of their insolubility in water of $\text{pH} > 5$. However, substantial chromium toxicity is expected if incinerator ashes contain Cr and Mn as co-contaminants. Oxides of manganese are capable of direct conversion of Cr^{+3} to Cr^{+6} (12). Chromium in the +6 oxidation state (chromate) differs from that in the +3 state in that it is quite soluble in water and exhibits bioavailability to plants equivalent to orthophosphate (13). Chromate (CrO_4^{-2}) is in equilibrium with bi-chromate (HCrO_4^-) and di-chromate ($\text{Cr}_2\text{O}_7^{-2}$) with the latter forms increasing in concentration at $\text{pH} < 6$ (12). It is important to note that chromates and dichromates are potent oxidizers of organic material and additions of Cr^{+6} compounds to organic rich soil results in conversion to Cr^{+3} forms (13). Chromium in the plus III and the plus IV oxidation states forms strong complexes with natural ligands in the organic fraction of soils (13). Therefore, chromium is available for leaching and uptake by plants only when it is present in the unbound form in the plus VI oxidation state.

Ligand Formation

In addition to the direct effects, incineration can alter the bioavailability and leachability of metals by destruction of the functional groups in the soil which are responsible for binding cations. High temperature combustion of soils under oxidative conditions converts organic compounds in soil into more oxidized products. Sulfur in the form of sulfhydryls (mercaptans) is converted to gaseous sulfur dioxide. Naturally occurring amines are oxidized to nitric oxide, and carboxylic acids become CO_2 . These oxidations virtually eliminate ligand binding sites which are responsible for much of the retention of toxic metals in soil.

Oxidation of toxic metals and destruction of centers for chelation have the potential of increasing both the mobility and bioavailability of these compounds. However, it is important to avoid comparison of the leaching potential of metals in sediments in wastewater to those in sediments from healthy impoundments. Water-covered sediments often generate reducing conditions due to the action of facultative anaerobes. Metals in these sediments can often be found in lower oxidation states than those in environments which are in equilibrium with atmospheric oxygen, and cation exchange capacity in healthy sediments is high. Thus the leaching potential of metals is decreased by the presence of a healthy microbial flora. However, healthy microbial flora are not seen in Army waste water lagoons because populations are decimated by the toxicity of the anthropogenic compounds present.

Discussion

Important factors that must be considered in selecting a remediation method are the amount of contamination, the method of disposal of the treated materials, and the regulations that govern the operation. Destruction of a contaminant is superior to modifying or immobilizing it, and environmental regulations are evolving toward remedies that permanently reduce the toxicity and volume of hazardous wastes. The Superfund Amendments and Reauthorization Act (SARA) was sent to EPA with a mandate from congress to permanently decrease the toxicity, mobility, and volume of hazardous wastes. Environmental restorations at military reservations are not funded by the SARA trust fund but Section 120 of SARA ("Federal Facilities Compliance Strategy") mandates federal facilities adherence to all provisions of this document.

Remediation methods like soil washing and composting, which produce secondary wastes, and "containment methods" such as solidification may require land filling of material which contains substantial concentrations of the target pollutant. Direct biological remediation of grossly contaminated soil is probably not feasible because much of the explosive is sequestered in insoluble crystals and because explosive compounds in high concentration are toxic to microorganisms. Excavation and land-fill of explosive contaminated soil at off-site facilities can be used as a method of remediation. However, high concentrations of explosive will cause the soil to be classified as a hazardous waste.

The Department of Transportation (DOT) and RCRA laws that govern the movement of hazardous waste are complex. If the wastes are transported across state lines, additional impediments may be emplaced by the receiving state. Thus, transport and land fill of hazardous wastes becomes a costly practice that requires substantial administrative effort and increased environmental liability. Moreover, because the waste is not destroyed, the installation remains potentially responsible for cleanup costs if the landfill is later closed and reclaimed. The liability for cleanup remains even if the waste is transferred to a hazardous waste contractor prior to land filling (CFR 40 264.147).

Since explosive compounds can essentially be eliminated from soil by incineration, this method is superior to the above methods for remediation of explosive-contaminated sites. Because cleanup standards are set to reflect the best currently available methods, levels of cleanup may be required that can only be achieved by incineration (55 FED Reg 30822). However, the cost of incineration is high (\$200/ton to \$1000/ton), and the procedure must be used selectively (14).

Incineration may be carried out with an on-site mobile or transportable unit, or the soil may be sent to a hazardous waste unit off base. On-site incineration has several advantages to the Army. Incineration at the AOC will eliminate the cost and permitting requirements for hauling the material off the installation. In addition, RCRA land disposal laws stipulate that if the waste is consolidated from different AOCs into a single AOC or moved outside of an AOC for treatment, and returned to the same or different AOC, testing is required to ensure that the material was not cross-contaminated with toxic ash

from other sources. More lenient statutes apply if the material is excavated and incinerated, and the ash redeposited, without leaving the AOC. Sites which are remediated under SARA stipulate that incineration performed within the AOC does not require state and local permits.

Potential cost advantages may also be obtained if the site can be designated as a "Corrective Action Management Unit" which could relax certain regulations to promote the cleanup process (55 FED REG 30851 and proposed 40 CFR 264.530). In addition, RCRA authority can impose a "conditional remedy", which means an AOC may be cleaned only to a level sufficient to support its current use. The flexibility that is present in this program is available only if the facility is currently operating under RCRA permit and therefore can be expected to demonstrate a quicker response and better control of problems. This flexibility does not extend to RCRA mandated remediations which are performed in association with the closing of an installation.

The lack of analytical determinations for the presence of PAH compounds is a shortcoming of current remediation projects. Substantial amounts of soils are incinerated during remediation of pink water lagoons, and the possibility for production of PAHs during incineration should be examined. It is probable that the rigorous reaction conditions reported as optimal (4), if maintained throughout processing, would prevent the formation of hazardous organic compounds. However, current soil incineration projects are operating without electronic monitoring of O_2 , NO_x , and CO in the primary kiln and oxygen partial pressures are low. The Record of Decision for remediation of the explosive contaminated soil at the Savanna Army Depot Activity, requires only 3% oxygen in the exhaust, and this is measured at the exhaust stack. A 3% level "at the stack" is indicative of a near zero level in the primary combustion chamber because additional air enters the system in the cyclone fly ash removal system and in the secondary combustion chamber.

Therefore, the primary combustion chamber of the incinerator is operated at oxygen levels which are likely to produce PICs and systems are lacking which would detect these in the primary combustion chamber or in the incinerated soil. Future incineration operations should require analysis of the treated soil for PAHs. If PAHs are found, the incinerator should thereafter be operated with greater amounts of oxygen and the concentrations of O_2 , CO_2 and CO should be monitored by electronic sensing in the rotary kiln. High levels of O_2 and a high ratio of CO_2/CO would provide a real-time mechanism to assess combustion conditions and thus ensure operators that PAHs are not being generated.

Contaminated sediments at pink water lagoons sometimes contain concentrations of explosive which make excavation and incineration of sediment hazardous. Sediments that contains over 12% TNT may propagate an explosion over the extent of their mass, but less concentrated sediments produce only localized explosions. Army regulation 385-66 states "An action level of < 10% explosive is used by the Army to delineate a non-explosive operation in which a propagated detonation is unlikely. Operations classified as explosive require approval of the DOD Explosive Safety Board". In an effort to minimize the hazard of explosion, less contaminated deeper soils are often blended with more contaminated surface soils usually while the area is underwater. Mixing

is accomplished by repetitively scooping and dumping sediments with a floating dredge. This process is effective from a safety standpoint but eliminates organic rich, high CEC content soil layers from the AOC.

Soil that is lost to incineration is routinely replaced with clean fill. Under current procedures, incinerated soils are normally returned directly to the area of excavation. This practice minimizes requirements for clean fill but may be environmentally unsound because of the diminished cation exchange capacity of the incinerated soils (discussed above). Although all sites remediated thus far have had concentrations of metals in the incinerated soil that were below those which would characterize it as hazardous waste, the TCLP test may not be indicative of the environmental impact of metals in incinerated soils. Incinerated soils initially contain substantial alkalinity due to the presence of oxides of alkaline earths (quick lime). Leaching with acidic precipitation will eventually expended the alkalinity and the pH of the leaching solution will decrease. Decreases in the pH of the leaching solution will result in increased leaching of toxic metals due to changes in solubility and ligand binding potential.

Changes in solubility may also be produced by localized variations in the environment. Metals will often form compounds which reflect the reduction potential of their surroundings (15). Thus, a highly reduced land fill environment would probably produce different suite of compounds than would an environment than is in equilibrium with air.

It is therefore important to discard ash which contains toxic metals in a manor which minimizes unwanted chemical transformation and leaching behavior. An additional step, in which the incinerated soil is tilled into pasture soil of high CEC, would accomplish these goals and should be considered in future remediations

The EPA is in the process of issuing new regulations that may effect the remediation process. The regulations sited in this document reflect the current legal environment but changes are likely. In their pre-publication review of this manuscript (16) the EPA recommended that contractors should contact the EPA and the appropriate state agencies during the planing phases of a remediation to ensure the most recent regulations complied with.

REFERENCES

1. Noland, J.W., and W.E. Sisk. 1984. Incineration of Explosives Contaminated Soils. U.S. Army Contractors Report. AD-P004 142.
2. Installation Restoration Incineration Program DRAFT Final Report on Decontamination Operations at the Louisiana Army Ammunition Plant. Nov. 1990. Report Prepared by the International Technology Corporation for the U.S. Army Corps of Engineers under Contract No. DACA45-87-C0103.
3. Rey de Castro, B. 1989. Movable Hazardous Waste Incinerators, Part I, A Big Role For Rolling Incinerators. Waste Age. vol 1, 98-104.
4. Noland, J.W., J.R. Marks, and P.J. Marks. 1984. Incineration Test of Explosives Contaminated Soils At Savanna Army Depot Activity, Savanna Illinois. Contractor report. AD A140155.
5. Manahan S.E. 1990. Environmental Chemistry, 4th Edition. Columbia, MO: Lewis Publishers.
6. Brueggemann, E.E. 1986. Liquid chromatographic determination of explosives and polynuclear aromatic hydrocarbons (PAHs) in deactivation furnace ash. Technical Report No. 8604. AD-A171269.
7. Bailar, J.C. Jr, H.J. Emeleus, R. Nyholm, and A.F. Trotman-Dickenson, Editorial Board, 1973. Comprehensive Inorganic Chemistry, vol 1. Elmsford, NY: Pergamon Press.
8. Puglionesi, P.S., J. Kesari, and M.H. Corbin. 1988. Treatment of heavy metals coils by roasting. In Proceedings of the 13th annual environmental quality R&D symposium, 150-61. Aberdeen Proving Ground, MD: U.S. Army Toxic Hazardous Materials Agency
9. Lindberg, S.E. 1980. Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms. Atmospheric Environment, vol 14, 227-31.
10. Bailar, J.C. Jr, H.J. Emeleus, R. Nyholm, and A.F. Trotman-Dickenson, Editorial Board, 1973. Comprehensive Inorganic Chemistry, vol 2. Elmsford, NY: Pergamon Press.
11. The Merck Index 11th Edition. 1989. S. Budavari, M.J. O'Neil, A. Smith, P.E. Heckelman, Editorial Board. Rahway, NJ: Merck & Co.
12. Bailar, J.C. Jr, H.J. Emeleus, R. Nyholm, and A.F. Trotman-Dickenson, Editorial Board, 1973. Comprehensive Inorganic Chemistry, vol 3. Elmsford, NY: Pergamon Press.
13. Smith, S., P.J. Peterson, and K.H.M. Kwan. 1989. Chromium Accumulation, Transport and Toxicity in Plants. Toxicological and Environmental Chemistry, Vol 24, 241-51.

14. Reeves, T.C. 1991. On-site incineration of contamination soil: a study into U.S. Navy Applications. U.S. Navy technical report. AD A241315.
15. Swartzbaugh, J., J. Sturgill, H.D. Williams, and B. Cormier. 1992. Remediating Sites Contaminated with Heavy Metals. Hazardous Materials Control, vol 11, 36-46.
16. Letter dated 19 Nov 92 from Douglas A. Donor, LDR Program Manager PA Permits Section, The U.S. Environmental Protection Agency Region 111, Philadelphia, PA.

GLOSSARY

Area of Contamination (AOC)
Cornhusker Army Ammunition Plant (CAAP)
Cation Exchange Capacity (CEC)
Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)
Corrective Measures Study (CMS)
Corrective Measure Implementation (CMI)
Destruction and Removal Efficiency (DRE)
Department of Transportation (DOT)
Engineering Evaluation/Cost Analysis (EE/CA)
Louisiana Army Ammunition Plant (LAAP)
National Priorities List (NPL)
Preliminary Assessment (PA)
Polycyclic Aromatic Hydrocarbons (PAH)
Products of Incomplete Combustion (PIC)
Point of Compliance (POC)
Principal Organic Hazardous Constituents (POHC)
Quality Assurance Project Plan (QAPP)
Resource Conservation and Recovery Act (RCRA)
RCRA Facility Assessment (RFA)
RCRA Facility Investigation (RFI)
Remedial Investigation/Feasibility Study (RI/FS)
Superfund Amendments and Reauthorization Act (SARA)
Toxicity Characteristic Leaching Procedure (TCLP)

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